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Preliminary communication

SYNTHESIS, STABILITY AND PROPERTIES OF PHENYLALUMINIUM TETRAHYDROBORATES

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Summary

Triphenylalane dissolves readily in aluminium tris(tetrahydroborate) to yield the solid dimeric compound Ph_2AlBH_4. The monophenyl derivative is unstable and could not be isolated pure in contrast with the corresponding alkyl compounds where the monomeric monoalkyl derivative, $RAl(BH_4)_2$, is the more stable. Ph_2AlBH_4 forms 1/1 adducts with Et_2O and NMe_3, but the latter undergoes a rearrangement reaction yielding Ph_2AlH and H_3BNMe_3.

We have recently been investigating exchange reactions among organometallic compounds of the main group elements [1,2] including reactions of trialkyl alanes with aluminium tris(tetrahydroborates) in order to determine the relative stabilities and association of such compounds. In the alkyl series $R_xAl(BH_4)_{3-x}$, (R = Me, Et, n-Pr, i-Bu; x = 1 or 2), it is the monoalkyl derivatives which are the more stable with the dialkyl compounds disproportionating at ambient temperatures [3].

$$2R_2Al(BH_4) \rightarrow RAl(BH_4)_2 + AlR_3$$

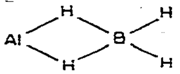
In the case of the n-propyl and i-butyl compounds, the rate of disproportionation is so rapid that the pure compounds (R_2AlBH_4) cannot be isolated. The presence of the tetrahydroborate group stabilises all of these compounds in the monomeric state, whereas the corresponding straight chain trialkylalanes (Al_2R_6, R = Me or Et) are dimeric.

We have now found that an interesting reversal of the above stabilities arises with the phenyl derivatives in that when triphenylalane is mixed with aluminium tris(tetrahydroborate), either in toluene or in the absence of solvent, in a variety of stoichiometric ratios, only the diphenylaluminium tetrahydroborate can be isolated as a white crystalline solid.

$$Al_2Ph_6 + Al(BH_4)_3 \rightarrow 3Ph_2AlBH_4$$

Attempts to isolate $PhAl(BH_4)_2$, by mixing the two reagents in the appropriate 1/2 molar ratio, afforded a white solid contaminated with a liquid which was removed by pumping in vacuo and shown to be $Al(BH_4)_3$, while the solid remaining was $Ph_2Al(BH_4)$.

Cryoscopic measurements in benzene show that Ph_2AlBH_4 is 55% associated whereas $AlPh_3$ itself is 80% associated under similar conditions [4]. Thus, while the tetrahydroborate group does affect the properties of the bridging Al—$(Ph)_2$—Al system, its effect is considerably less than with the alkyl compounds. This is in accord with other observations that the stability of Al—Ph—Al bridges with respect to dissociation is generally greater than those of methyl or ethyl bridged dimers [5,6]. Ph_2AlBH_4 is soluble in benzene and toluene, but may be sublimed only with difficulty above 100°C when extensive decomposition occurs yielding a grey-black residue. In order to obtain a pure sample it is most convenient to start with pure Al_2Ph_6 and $Al(BH_4)_3$ mixed in the appropriate molar ratio. It is stable under nitrogen at room temperature, but on prolonged standing under vacuum slowly evolves hydrogen. The IR spectrum is consistent with the presence of terminal



groups, and bridging phenyl groups, showing terminal B—H stretching frequencies at 2460 and 2410 cm^{-1} with a Al—H—B bridge mode at 2150 cm^{-1}. The fluxional behaviour of the protons in the BH_4 group, observed in other Al—BH_4 derivatives [2], is also preserved in Ph_2AlBH_4 so that the ^1H and ^{11}B NMR spectra of 25°C show broad signals which resolve into a 1/1/1/1 quartet at 75°C and a 1/4/6/4/1 quintet, respectively (Table 1).

As with triphenylalane itself, Ph_2AlBH_4 reacts rapidly with ligands (e.g. Et_2O and NMe_3) forming 1/1 colourless solid adducts, although the NMe_3 adduct is different from those with alkylaluminium derivatives in that it decomposes within a few hours at 25°C under nitrogen, liberating H_3BNMe_3 and Ph_2AlH. Such instability probably arises from steric crowding around the aluminium atom since the corresponding ether adduct is stable under these conditions.

TABLE 1

CHEMICAL SHIFT VALUES FOR VARIOUS ALUMINIUM TETRAHYDROBORATE COMPOUNDS

Compound	Solvent	$\delta(^1H)$ (ppm)[a]	$\delta(^{11}B)$ (ppm)[b]
Ph_2AlBH_4	C_7D_8[c]	0.99[d]	—34.2
$Al(BH_4)_3$		0.70	—35.5
$Ph_2AlBH_4 \cdot Et_2O$	C_6D_6	1.37	—39.7
$Ph_2AlBH_4 \cdot NMe_3$	C_6D_6	1.27	—38.9[e]

[a] ^1H shifts rel. to TMS = 0 ppm, downfield shifts are positive. [b] ^{11}B shifts rel. to $BF_3 \cdot Et_2O$ = 0 ppm, downfield shifts are positive. [c] C_7D_8 = deuterotoluene, C_6D_6 = deuterobenzene. [d] Broad signal, shift corresponds to centre. [e] Poorly resolved quintet due to decomposition in solution.

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